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(54) Title: AUTOMATIC DISHWASHING COMPOSITIONS CONTAINING ALUMINUM SALTS		
(57) Abstract A composition for inhibiting lead corrosion of fine tableware washed in automatic dishwashers is disclosed. The composition comprises an aluminum salt which dissolves at a rate to deliver less than 0.56 mM aluminum (III) per minute at 42 °C to a wash liquor, a bleaching agent, a builder and optionally a surfactant. The composition has a pH of less than about 10 is substantially free of silicates.		

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AUTOMATIC DISHWASHING COMPOSITIONS
CONTAINING ALUMINUM SALTS

5

FIELD OF THE INVENTION

This invention relates to automatic dishwashing detergent compositions containing an aluminum species which inhibits corrosion of fine tableware.

10

BACKGROUND OF THE INVENTION

It is well known in the art that automatic dishwashers corrode glassware particularly when cleaned with highly
15 alkaline detergent compositions. See Newton, R. G., The Durability of Glass-A Review, Glass Technology Vol. 26 No. 1, February 1985, pp. 21-38 and US 4,933,101 (Cilley et al.). The visible forms of glassware corrosion are generally caused by hydrolysis and therefore dissolution of the glassware's
20 silicate network. This dissolution is known to be very low at pH values below 9.5 and increases with increasing pH (see Kruger, A. A., The Role of the Surface on Bulk Physical Properties of Glasses, in Surface and Near-Surface Chemistry of Oxide Materials, eds. Nowotny, J., and Dufour, L.-C., pp.
25 413-448). Thus detergent compositions having an alkalinity of less than about pH 10 were conventionally believed to exert very low corrosivity towards glassware.

Cleaning restrictions forced prior art formulators to
30 seek solutions to tableware corrosion while maintaining high alkalinity in detergent products. The art teaches that silicate in combination with fast dissolving aluminum salts avoids high alkalinity corrosion of glassware.. See US

3,350,318, issued on October 31, 1967 to Green and US
3,255,117 issued June 7, 1966 to Knapp et al.

As detergent compositions have increasingly become based
5 on enzymes allowing the products to be milder and more
environmentally friendly, it was believed that glassware
corrosion would not be a problem especially at pH values of
less than about 10.

10 It has now been discovered that detergent formulations
having neutral pH or low alkalinity significantly corrode
fine tableware, particularly lead crystal glassware. It is
believed that the lead and boron minerals of the tableware
take part in the formation of the silicate network. When
15 such minerals are extracted the silicate network falls apart
readily. This corrosion is especially pronounced in the
absence of silicate which is not always incorporated in low
alkalinity or neutral pH products. It has further been
observed that detergent compositions incorporating aluminum
20 salts to inhibit corrosion compromise cleaning and leave
significant stains on washed tableware.

It has been surprisingly discovered that by utilizing
certain slow dissolving aluminum salts in automatic
25 dishwashing compositions that tableware corrosion can be
inhibited and that cleaning efficiency can be improved.

It has also been surprisingly discovered that by
utilizing certain sequestrants in combination with any water
30 soluble aluminum salt that both tableware corrosion and the
negative impact on cleaning efficiency can be minimized.

It is thus an object of the present invention to provide
improved pH-neutral to mildly alkaline automatic dishwashing

detergent compositions which not only protect against tableware corrosion but also provide good cleaning performance in removing stains from tableware.

5 Another object of the invention is to provide a process for incorporating aluminum salts in automatic dishwashing detergent compositions to provide effective cleaning performance without tableware corrosion. Although the preparation of the compositions containing the slow
10 dissolving aluminum salts may be by any conventional method, a premix of aluminum-sequestrant complexes must be prepared before the remaining components are added to form the aluminum-sequestrant compositions.

15 SUMMARY OF THE INVENTION

The compositions of the invention are automatic dishwashing detergent compositions which substantially inhibit lead corrosion of fine tableware, comprising:

20

a) 0.01 to 25 wt. %, preferably 1 to 15, of an aluminum salt which dissolves at a rate to deliver less than 0.56 mM aluminum(III) per minute at 42°C to a wash liquor ;

25 b) 1 to 20 wt. % of a bleaching agent selected from a peroxygen agent, hypohalite agent, corresponding salts and mixtures thereof;

30

c) 1 to 75 wt. % of a builder, and

d) 0 to 40 wt. % of a surfactant,

a 1% aqueous solution of the detergent composition having a pH of less than 10 and being substantially free of added silicates.

5 In view of its low rate of dissolution, the aluminum salt of the invention is characterised by controlled release of aluminum(III) ions from the product to the surface of the tableware. The aluminum salt may be part of an aluminum-sequestrant complex in which the aluminum is bound by a
10 sequestrant, said complex preventing for at least one hour, the precipitation of any aluminum compound from an aqueous solution having a pH in the range of from 7 to 10.

The compositions of the invention may be in any variety
15 of physical forms, namely, liquid, powder or gel.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The compositions of the invention are effective cleaners
20 which do not corrode tableware, particularly tableware for entertainment or decorative purposes. Such glassware generally has a high refractive index which gives the classic "sparkle" when cut into decorative shapes. For purposes of this invention, the lead content of such tableware is more
25 than about 20% by weight.

Slow Dissolving Aluminum Salts

The term "slow dissolving aluminum salt" refers to an
30 aluminum salt that dissolves at a rate to yield less than 0.56 mM aluminum(III) per minute at 42°C.

Slow dissolving aluminum salts within the scope of the invention include: aluminum stearate, aluminum tartrate,

aluminum acetate, aluminum acetotartrate, aluminum salicylate, aluminum bis(acetylsalicylate), aluminum formate, aluminum octoate, aluminum borate, aluminum oleate, aluminum palmitate, aluminum acetylacetonate, aluminum phosphate and mixtures thereof. Preferred aluminum salts include aluminum acetate, aluminum acetylacetonate, aluminum octoate and aluminum phosphate. Most preferred aluminum salts include aluminum acetate, aluminum acetylacetonate and aluminum octoate.

10

The aluminum salt should be incorporated in the detergent composition in an amount to deliver 0.1 mM to 10 mM, preferably 0.5 mM to 5 mM, most preferably 1 mM to 2 mM Al(III) in the wash.

15

Aluminum-Sequestrant Complexes

The term "aluminum-sequestrant complex" refers to a system containing an aluminum salt and a sequestrant which, when prepared properly, results in a reduced release rate of Al(III) ions.

20

Aluminum salts useful to form the aluminum-sequestrant complexes within the scope of the invention include: aluminum sulfate, sodium aluminate, aluminum acetate, aluminum acetylacetonate, aluminum formate, aluminum borate, aluminum octoate, aluminum oleate, aluminum palmitate, aluminum tartrate, aluminum acetotartrate, and mixtures thereof. Preferred aluminum salts include: aluminum sulfate, sodium aluminate, aluminum acetate, aluminum acetylacetonate, and aluminum borate. Most preferred aluminum salts include: aluminum sulfate, sodium aluminate, and aluminum acetylacetonate.

30

Sequestrants within the scope of the invention include the following acids and their alkali metal salts: EDTA, oxalic acid, citric acid, cyanuric acid, NTA, sodium orthophosphoric acid, malonic acid, succinic acid, tartaric acid, aspartic acid, glutamic acid, phosphonic acid, and polyphosphoric acid. Preferred sequestrants include: EDTA, oxalic acid, sodium citrate, and cyanuric acid. Most preferred sequestrants include: sodium citrate, oxalic acid, and cyanuric acid.

10

The aluminum-sequesterant complex is prepared as follows: with stirring, the desired amount of the selected sequesterant is added to water. During dissolution of the sequesterant, the pH of the solution is adjusted with an inorganic acid, or an inorganic base, preferably NaOH or H₂SO₄, to a pH of not less than one pH unit above the pK_a of at least one of the ionizable groups on the sequesterant. This mixture is allowed to stir until the sequesterant is completely dissolved. The aluminum salt is dosed into the solution of the sequesterant and allowed to dissolve. During the dissolution of the aluminum salt, the pH of the system is adjusted to the same pH as during the initial dissolution of the sequesterant with NaOH or H₂SO₄, as necessary. After the aluminum salt is completely dissolved, the complex is ready for use.

25

Alkalinity

The alkalinity of a 1% aqueous solution of the compositions of the invention should be neutral to low alkalinity, being less than a pH of 10, more preferably 7 to 9. Maintenance of the composition's pH within the desired range provides stain removal while inhibiting corrosion of fine tableware.

The aluminum salts can interact with tea stains so that the incorporation of slow dissolving aluminum salts in the compositions allows effective bleaching before substantial levels of Al(III) are released into the wash water.

5

In the aluminum-sequestrant complexes, on the other hand, the aluminum is bound to the sequestrant strongly enough to delay interaction of Al(III) with tea stains.

10

Any number of conventional buffer agents may be used to maintain the desired pH range. Such materials can include, for example, various water soluble inorganic salts such as the carbonates, bicarbonates, sesquicarbonates, silicates, pyrophosphates, phosphates, tetraborates and mixtures thereof.

The buffering agents should be present in the compositions in a amount of from about 2 to about 30 wt. %, preferably from 5 to about 25% by wt. of the total composition.

Detergent Builder Materials

The compositions of this invention can further contain all manner of detergent builders commonly taught for use in automatic dishwashing of compositions to increase the effectiveness of the detergent by in part, binding calcium salts to act as a softener. The builders can include any of the conventional inorganic and organic water-soluble builder salts, or mixtures thereof and may comprise 1 to 75%, and preferably, from about 5 to about 70% by weight of the cleaning composition.

Typical examples of phosphorus-containing inorganic builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates and polyphosphates. Specific examples of inorganic phosphate
5 builders include sodium and potassium tripolyphosphates, phosphates, pyrophosphates and hexametaphosphates.

Suitable examples of non-phosphorus-containing inorganic builders, when present, include water-soluble alkali metal
10 carbonates, bicarbonates, sesquicarbonates, borates, silicates, metasilicates, and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites.

15

Particularly preferred inorganic builders can be selected from the group consisting of sodium tripolyphosphate, potassium pyrophosphate, sodium carbonate, potassium carbonate, sodium bicarbonate, sodium silicate and
20 mixtures thereof. When present in these compositions, sodium tripolyphosphate concentrations will range from about 2% to about 40%; preferably from about 5% to about 30%. Sodium carbonate and bicarbonate when present can range from about 5% to about 50%; preferably from about 10% to about 30% by
25 weight of the cleaning compositions. Sodium tripolyphosphate and potassium pyrophosphate are preferred builders in gel formulations, where they may be used at from about 3 to about 30%, preferably from about 10 to about 20%.

30 Organic detergent builders can also be used in the present invention. Examples of organic builders include alkali metal citrates, succinates, malonates, fatty acid sulfonates, fatty acid carboxylates, nitrilotriacetates, phytates, phosphonates, alkanehydroxyphosphonates,

oxydisuccinates, alkyl and alkenyl disuccinates, oxydiacetates, carboxymethyloxy succinates, ethylenediamine tetraacetates, tartrate monosuccinates, tartrate disuccinates, tartrate monoacetates, tartrate diacetates, 5 oxidized starches, oxidized heteropolymeric polysaccharides, polyhydroxysulfonates, polycarboxylates such as polyacrylates, polymaleates, polyacetates, polyhydroxyacrylates, polyacrylate/polymaleate and polyacrylate/ polymethacrylate copolymers, 10 aminopolycarboxylates and polyacetal carboxylates such as those described in U.S. Patent Nos. 4,144,226 and 4,146,495.

Alkali metal citrates, oxydisuccinates, polyphosphates and acrylate/maleate copolymers are especially preferred 15 organic builders. When present they are preferably available from about 1% to about 35% of the total weight of the detergent compositions.

The foregoing detergent builders are meant to illustrate 20 but not limit the types of builders that can be employed in the present invention.

Surfactants

25 Useful surfactants include anionic, nonionic, cationic, amphoteric, zwitteronic types and mixtures of these surface active agents. Such surfactants are well known in the detergent art and are described at length in "Surface Active Agents and Detergents", Vol. II, by Schwartz, Perry & Birch, 30 Interscience Publishers, Inc. 1959, herein incorporated by reference.

Anionic synthetic detergents can be broadly described as surface active compounds with one or more negatively charged

functional groups. Soaps are included within this category. A soap is a C_8 - C_{22} alkyl fatty acid salt of an alkali metal, alkaline earth metal, ammonium, alkyl substituted ammonium or alkanolammonium salt. Sodium salts of tallow and coconut fatty acids and mixtures thereof are most common. Another important class of anionic compounds are the water-soluble salts, particularly the alkali metal salts, of organic sulfur reaction products having in their molecular structure an alkyl radical containing from about 8 to 22 carbon atoms and a radical selected from the group consisting of sulfonic and sulfuric acid ester radicals. Organic sulfur based anionic surfactants include the salts of C_{10} - C_{16} alkylbenzene sulfonates, C_{10} - C_{22} alkane sulfonates, C_{10} - C_{22} alkyl ether sulfates, C_{10} - C_{22} alkyl sulfates, C_4 - C_{10} dialkylsulfosuccinates, C_{10} - C_{22} acyl isothionates, alkyl diphenyloxide sulfonates, alkyl naphthalene sulfonates, and 2-acetamido hexadecane sulfonates. Organic phosphate based anionic surfactants include organic phosphate esters such as complex mono- or diester phosphates of hydroxyl-terminated alkoxide condensates, or salts thereof. Included in the organic phosphate esters are phosphate ester derivatives of polyoxyalkylated alkylaryl phosphate esters, of ethoxylated linear alcohols and ethoxylates of phenol. Also included are nonionic alkoxylates having a sodium alkylencarboxylate moiety linked to a terminal hydroxyl group of the nonionic through an ether bond. Counterions to the salts of all the foregoing may be those of alkali metal, alkaline earth metal, ammonium, alkanolammonium and alkylammonium types.

Nonionic surfactants can be broadly defined as surface active compounds with one or more uncharged hydrophilic substituents. A major class of nonionic surfactants are those compounds produced by the condensation of alkylene oxide groups with an organic hydrophobic material which may

be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. Illustrative, but not limiting examples, of various suitable nonionic surfactant types are:

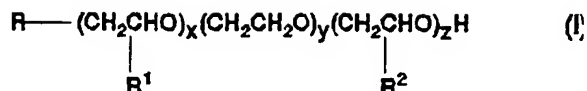
(a) polyoxyethylene or polyoxypropylene condensates of aliphatic carboxylic acids, whether linear- or branched-chain and unsaturated or saturated, containing from about 8 to about 18 carbon atoms in the aliphatic chain and incorporating from about 2 to about 50 ethylene oxide and/or propylene oxide units. Suitable carboxylic acids include "coconut" fatty acids (derived from coconut oil) which contain an average of about 12 carbon atoms, "tallow" fatty acids (derived from tallow-class fats) which contain an average of about 18 carbon atoms, palmitic acid, myristic acid, stearic acid and lauric acid,

20

(b) polyoxyethylene or polyoxypropylene condensates of aliphatic alcohols, whether linear- or branched-chain and unsaturated or saturated, containing from about 6 to about 24 carbon atoms and incorporating from about 2 to about 50 ethylene oxide and/or propylene oxide units. Suitable alcohols include "coconut" fatty alcohol, "tallow" fatty alcohol, lauryl alcohol, myristyl alcohol and oleyl alcohol. Particularly preferred nonionic surfactant compounds in this category are the "Neodol" type products, a registered trademark of the Shell Chemical Company.

30

Also included within this category are nonionic surfactants having a formula:

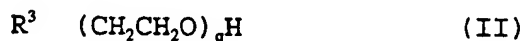


wherein R is a linear
 5 alkyl hydrocarbon radical having an average of 6 to 18 carbon atoms, R¹ and R² are each linear alkyl hydrocarbons of about 1 to about 4 carbon atoms, x is an integer of from 1 to 6, y is an integer of from 4 to 20 and z is an integer from 4 to 25.

10

One preferred nonionic surfactant of formula I is Poly-Tergent SLF-18[®] a registered trademark of the Olin Corporation, New Haven, Conn. having a composition of the above formula where R is a C₆-C₁₀ linear alkyl mixture, R¹ and
 15 R² are methyl, x averages 3, y averages 12 and z averages 16. Also suitable are alkylated nonionics as are described in U.S. Patent 4,877,544 (Gabriel et al.), incorporated herein by reference.

20 Another nonionic surfactant included within this category are compounds of formula:

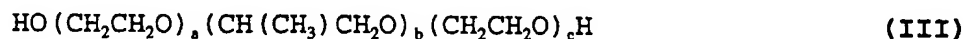


25 wherein R³ is C₆-C₂₄ linear or branched alkyl hydrocarbon radical and q is a number from 2 to 50; more preferably R³ is a C₈-C₁₈ linear alkyl mixture and q is a number from 2 to 15.

(c) polyoxyethylene or polyoxypropylene condensates of
 30 alkyl phenols, whether linear- or branched-chain and unsaturated or saturated, containing from about 6 to 12 carbon atoms and incorporating from about 2 to about 25 moles of ethylene oxide and/or propylene oxide.

(d) polyoxyethylene derivatives of sorbitan mono-, di-, and tri-fatty acid esters wherein the fatty acid component has between 12 and 24 carbon atoms. The preferred polyoxyethylene derivatives are of sorbitan monolaurate, sorbitan trilaurate, sorbitan monopalmitate, sorbitan tripalmitate, sorbitan monostearate, sorbitan monoisostearate, sorbitan tripalmitate, sorbitan monostearate, sorbitan monoisostearate, sorbitol tristearate, sorbitan monooleate, and sorbitan trioleate. The polyoxyethylene chains may contain between about 4 and 30 ethylene oxide units, preferably about 20. The sorbitan ester derivatives contain 1, 2 or 3 polyoxyethylene chains dependent upon whether they are mono-, di- or tri-acid esters.

(e) polyoxyethylene-polyoxypropylene block copolymers having formula:



or



wherein a, b, c, d, e and f are integers from 1 to 350 reflecting the respective polyethylene oxide and polypropylene oxide blocks of said polymer. The polyoxyethylene component of the block polymer constitutes at least about 10% of the block polymer. The material preferably has a molecular weight of between about 1,000 and 15,000, more preferably from about 1,500 to about 6,000. These materials are well-known in the art. They are available under the trademark "Pluronic" and "Pluronic R", a product of BASF Corporation.

(f) Alkyl glycosides having formula:

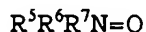


5 wherein R^4 is a monovalent organic radical (e.g., a monovalent saturated aliphatic, unsaturated aliphatic or aromatic radical such as alkyl, hydroxyalkyl, alkenyl, hydroxyalkenyl, aryl, alkylaryl, hydroxyalkylaryl, arylalkyl, alkenylaryl, arylalkenyl, etc.) containing from about 6 to
 10 about 30 (preferably from about 8 to 18 and more preferably from about 9 to about 13) carbon atoms; R^5 is a divalent hydrocarbon radical containing from 2 to about 4 carbon atoms such as ethylene, propylene or butylene (most preferably the unit $(R^5O)_n$ represents repeating units of ethylene oxide,
 15 propylene oxide and/or random or block combinations thereof); n is a number having an average value of from 0 to about 12; Z^1 represents a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms (most preferably a glucose unit); and p is a number having an average value of from 0.5
 20 to about 10 preferably from about 0.5 to about 5 .

Within the compositions of the present claim, alkyl polyglycosides will be present in amounts ranging from about 0.01 to about 20% by weight, preferably from about 0.5 to
 25 about 10%, optimally between about 1 and 5%.

Examples of commercially available materials from Henkel Kommanditgesellschaft Aktien of Dusseldorf, Germany include APG[®] 300, 325 and 350 with R^4 being C_9 - C_{11} , n is 0 and p is
 30 1.3, 1.6 and 1.8-2.2 respectively; APG[®] 500 and 550 with R^4 is C_{12} - C_{13} , n is 0 and p is 1.3 and 1.8-2.2, respectively; and APG[®] 600 with R^4 being C_{12} - C_{14} , n is 0 and p is 1.3. Particularly preferred is APG[®] 600.

(g) Amine oxides having formula:



(VI)

5 wherein R^5 , R^6 and R^7 are saturated aliphatic radicals or substituted saturated aliphatic radicals. Preferable amine oxides are those wherein R^5 is an alkyl chain of about 10 to about 20 carbon atoms and R^6 and R^7 are methyl or ethyl groups or both R^5 and R^6 are alkyl chains of about 6 to about 14
10 carbon atoms and R^7 is a methyl or ethyl group.

Amphoteric synthetic detergents can be broadly described as derivatives of aliphatic and tertiary amines, in which the aliphatic radical may be straight chain or branched and
15 wherein one of the aliphatic substituents contain from about 8 to about 18 carbons and one contains an anionic water-solubilizing group, i.e., carboxy, sulpho, sulphato, phosphato or phosphono. Examples of compounds falling within this definition are sodium 3-dodecylamino propionate and
20 sodium 2-dodecylamino propane sulfonate.

Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium and sulphonium compounds in which the aliphatic radical may
25 be straight chained or branched, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulpho, sulphato, phosphato or phosphono. These compounds are frequently referred to as
30 betaines. Besides alkyl betaines, alkyl amino and alkyl amido betaines are encompassed within this invention.

Silicates

If silicates are present in the compositions of the invention, they should be in an amount to provide neutral or low alkalinity (less than pH 10) of the composition.

Preferred amounts of silicates present should be from about 1 to about 5%. Especially preferred is sodium silicate in a ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ up from about 1.0 to about 3.3, preferably from about 2 to about 3.2.

Filler

10

An inert particulate filler material which is water-soluble may also be present in cleaning compositions in powder form. This material should not precipitate calcium or magnesium ions at the filler use level. Suitable for this purpose are organic or inorganic compounds. Organic fillers include sucrose esters and urea. Representative inorganic fillers include sodium sulfate, sodium chloride and potassium chloride. A preferred filler is sodium sulfate. Its concentration may range from 0% to 60%, preferably from about 10% to about 30% by weight of the cleaning composition.

Thickeners and Stabilizers

Thickeners are often desirable for liquid cleaning compositions. Thixotropic thickeners such as smectite clays including montmorillonite (bentonite), hectorite, saponite, and the like may be used to impart viscosity to liquid cleaning compositions. Silica, silica gel, and aluminosilicate may also be used as thickeners. Salts of polyacrylic acid (of molecular weight of from about 300,000 up to 6 million and higher), including polymers which are cross-linked may also be used alone or in combination with other thickeners. Use of clay thickeners for automatic dishwashing compositions is disclosed for example in U.S.

Patent Nos. 4,431,559; 4,511,487; 4,740,327; 4,752,409. Commercially available synthetic smectite clays include Laponite supplied by Laporte Industries. Commercially available bentonite clays include Korthix H and VWH ex
5 Combustion Engineering, Inc.; Polargel T ex American Colloid Co.; and Gelwhite clays (particularly Gelwhite GP and H) ex English China Clay Co. Polargel T is preferred as imparting a more intense white appearance to the composition than other clays. The amount of clay thickener employed in the
10 compositions is from 0.1 to about 10%, preferably 0.5 to 5%. Use of salts of polymeric carboxylic acids is disclosed for example in UK Patent Application GB 2,164,350A, U.S. 4,859,358 and U.S. 4,836,948.

15 For liquid formulations with a "gel" appearance and rheology, particularly if a clear gel is desired, a chlorine stable polymeric thickener is particularly useful. U.S. Patent No. 4,260,528 discloses natural gums and resins for use in clear autodish detergents, which are not chlorine
20 stable. Acrylic acid polymers that are cross-linked manufactured by, for example, B.F. Goodrich and sold under the trade name "Carbopol" have been found to be effective for production of clear gels, and Carbopol 940 and 617, having a molecular weight of about 4,000,000 is particularly preferred
25 for maintaining high viscosity with excellent chlorine stability over extended periods. Further suitable chlorine-stable polymeric thickeners are described in U.S. Patent No. 4,867,896 incorporated by reference herein.

30 The amount of thickener employed in the compositions is from 0 to 5%, preferably 0.5-3%.

Stabilizers and/or co-structurants such as long chain calcium and sodium soaps and C₁₂ to C₁₈ sulfates are detailed

in U.S. Patent Nos. 3,956,158 and 4,271,030 and the use of other metal salts of long chain soaps is detailed in U.S. Patent No. 4,752,409. Other co-structurants include Laponite and metal oxides and their salts as described in U.S. 5 4,933,101, herein incorporated by reference. The amount of stabilizer which may be used in the liquid cleaning compositions is from about 0.01 to about 5% by weight of the composition, preferably 0.01-2%. Such stabilizers are optional in gel formulations. Co-structurants which are 10 found especially suitable for gels include trivalent metal ions at 0.01-4% of the compositions, Laponite and/or water-soluble structuring chelants at 1-60%. These co-structurants are more fully described in the co-pending U.S. Patent 5,141,664 by Corring et al., filed December 30, 15 1987, which application is hereby incorporated by reference.

Defoamer

The formulations of the cleaning composition comprising surfactant may further include a defoamer. Suitable 20 defoamers include mono- and distearyl acid phosphate, silicone oil and mineral oil. Even if the cleaning composition has only defoaming surfactant, the defoamer assists to minimize foam which food soils can generate. The compositions may include 0.02 to 2% by weight of defoamer, or 25 preferably 0.05-1.0%.

Minor amounts of various other components may be present in the cleaning composition. These include bleach scavengers including but not limited to sodium bisulfite, sodium 30 perborate, reducing sugars, and short chain alcohols; solvents and hydrotropes such as ethanol, isopropanol and xylene sulfonates; flow control agents (in granular forms); enzyme stabilizing agents; soil suspending agents; antiredeposition agents; anti-tarnish agents; anti-corrosion

agents; colorants; other functional additives; and perfume. The pH of the cleaning composition may be adjusted by addition of strong acid or base. Such alkalinity or buffering agents include sodium carbonate and sodium borate.

5

Enzymes

Enzymes capable of facilitating the removal of soils from a substrate may also be present in the invention in an amount of from 0 to 10 weight percent, preferably 1 to 5 weight percent. Such enzymes include proteases (e.g., Alcalase[®], Savinase[®] and Esperase[®] from Novo Industries A/S), amylases (e.g., Termamyl[®] from Novo Industries), and lipases (e.g., Lipolase[®] from Novo Industries).

15 Bleaching Agent

A wide variety of halogen and peroxygen bleach sources may be used in the present invention. Examples of such halogen and peroxygen bleaches are described in US Patent No. 5,200,236 issued to Lang et al., herein incorporated by reference.

Among suitable reactive chlorine or bromine oxidizing materials are heterocyclic N-bromo and N-chloro imides such as trichloroisocyanuric, tribromoisocyanuric, 25 dibromoisocyanuric and dichloroisocyanuric acids, and salts thereof with water-solubilizing cations such as potassium and sodium. Hydantoin compounds such as 1,3-dichloro-5,5-dimethylhydantoin are also quite suitable.

30 Dry, particular, water-soluble anhydrous inorganic salts are likewise suitable for use herein such as lithium, sodium or calcium hypochlorite and hypobromite. Chlorinated trisodium phosphate is another core material. Chloroisocyanurates are, however, the preferred bleaching

agents. Potassium dichloroisocyanurate is said by Monsanto Company as ACL-59*. Sodium dichloroisocyanurates are also available from Monsanto as ACL-60*, and in the dihydrate form, from the Olin Corporation as Clearon CDB-56*, available
5 in powder form (particle diameter of less than 150 microns); medium particle size (about 50 to 400 microns); and coarse particle size (150-850 microns). Very large particles (850-1700 microns) are also found to be suitable for encapsulation.

10

Peroxy Bleaching Agent

The oxygen bleaching agents of the compositions include organic peroxy acids and diacylperoxides. Typical monoperoxy
15 acids useful herein include alkyl peroxy acids and aryl peroxy acids such as:

(i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g., peroxy-alpha-naphthoic acid, and
20 magnesium monoperphthalate

(ii) aliphatic and substituted aliphatic monoperoxy acids, e.g., peroxy lauric acid, peroxy stearic acid, epsilon-phthalimido peroxyhexanoic acid and o-
25 carboxybenzamido peroxyhexanoic acid, N-nonenylamidoperadipic acid and N-nonenylamidopersuccinic acid.

Typical diperoxy acids useful herein include alkyl diperoxy acids and aryldiperoxy acids, such as:

30

(iii) 1,12-diperoxydodecanedioic acid

(iv) 1,9-diperoxyazelaic acid

(v) diperoxybrassylic acid; diperoxysebacic acid and diperoxy-isophthalic acid

(vi) 2-decyldiperoxybutane-1,4-dioic acid

(vii) N,N'-terephthaloyl-di(6-aminopercaproic acid).

A typical diacylperoxide useful herein includes dibenzoylperoxide.

Inorganic peroxygen compounds are also suitable for the present invention. Examples of these materials useful in the invention are salts of monopersulfate, perborate monohydrate, perborate tetrahydrate, and percarbonate.

Preferred oxygen bleaching agents include epsilon-phthalimido-peroxyhexanoic acid, o-carboxybenzamidoperoxyhexanoic acid, and mixtures thereof.

The oxygen bleaching agent is present in the composition in an amount from about of 1 to 20 weight percent, preferably 1 to 15 weight percent, most preferably 2 to 10 weight percent.

The oxygen bleaching agent may be incorporated directly into the formulation or may be encapsulated by any number of encapsulation techniques known in the art to produce stable capsules in alkaline liquid formulations.

A preferred encapsulation method is described in U.S. 5,200,236 issued to Lang et al., herein incorporated by reference. In the patented method, the bleaching agent is encapsulated as a core in a paraffin wax material having a

melting point from about 40°C to about 50°C. The wax coating has a thickness of from 100 to 1500 microns.

Bleach Precursors

5

Suitable peroxygen peracid precursors for peroxy bleach compounds have been amply described in the literature, including GB Nos. 836,988; 855,735; 907,356; 907,358; 907,950; 1,003,310 and 1,246,339; U.S. Pat. Nos. 3,332,882
10 and 4,128,494.

Typical examples of precursors are polyacylated alkylene diamines, such as N,N,N',N'-tetraacetylene diamine (TAED) and N,N,N',N'-tetraacetylmethylene diamine (TAMD);
15 acylated glycolurils, such as tetraacetylglycoluril (TAGU); triacetylcyanurate, sodium sulphophyl ethyl carbonic acid ester, sodium acetyloxybenzene sulfonate (SABS), sodium nonanoyloxy benzene sulfonate (SNOBS) and choline sulfophenyl carbonate. Peroxybenzoic acid precursors are
20 known in the art, e.g., as described in GB-A-836,988. Examples of suitable precursors are phenylbenzoate; phenyl p-nitrobenzoate; o-nitrophenyl benzoate; o-carboxyphenyl benzoate; p-bromo-phenylbenzoate; sodium or potassium benzoyloxy benzene-sulfonate; and benzoic anhydride.

25

Preferred peroxygen bleach precursors are sodium p-benzoyloxybenzene sulfonate, N,N,N',N'-tetraacetylene diamine, sodium nonanoyloxybenzene sulfonate and choline sulfophenyl carbonate.

30

Process

The compositions containing the slow dissolving aluminum salts as defined herein may be prepared in any conventional

manner known in the art to form any variety of physical forms of the compositions.

For the compositions containing the aluminum-sequestrant complex, it is essential that a premix of the sequestrant material and the aluminum salt be prepared prior to the incorporation of other components of the compositions of the invention. Once the premix is prepared, it may be processed with other detergent components in any conventional manner to form any variety of physical forms of automatic dishwashing detergent compositions, such as liquid, tablet, powder, gel.

To prepare the premix, the selected sequestrant should be completely dissolved in water to form a solution with a pH at least one pH unit greater than the pKa of at least one of the ionizable groups of the sequestrant. The pH must be maintained at this level during the entire dissolution step and the alkalinity of the solution may be adjusted by the addition of either an inorganic acid or an inorganic base, such as NaOH or H₂SO₄.

While maintaining the solution at a pH as described above, the selected aluminum salt is added to the solution and the pH is again adjusted to as close to the same pH as during the initial dissolution of the sequestrant as possible. Once the aluminum salt is dissolved into the sequestrant solution, the premix can be incorporated with other components to form the composition.

The following examples will serve to distinguish this invention from the prior art and illustrate its embodiments more fully. Unless otherwise indicated, all parts, percentages and proportions referred to are by weight.

Example 1

It was surprisingly observed that at low and neutral pH levels (less than about pH 10) lead mineral from lead containing glassware was more substantially extracted than at higher pH. Specifically, lead containing glass tiles
 5 obtained from Q-Glass, Inc. of Towaco, NJ and having a 50% lead content were soaked for 24 hours at 65°C in one liter soft water containing 6.8 grams of an automatic dishwashing composition having the following formula:

10	Ingredient	% of Active
	CDB capsules ¹	4.3
	Potassium tripolyphosphate	34
	Polymer ²	1
	Buffering agents	9
15	Non-ionic surfactant	2
	Potassium hydroxide (45% soln.)	1
	Enzymes	0.8
20	Water	to balance

The pH's of the four solutions were adjusted to 7.5, 8.6, 9.5, and 10.5 with NaOH and H₂SO₄. After soaking, the lead containing glass tiles and an aliquot of each detergent

¹Chlorine supplied as CDB-56, which is 56% available chlorine, and encapsulated according to US 5,200,236 issued to Lang et al. The resulting capsules are 50% CDB-56 and 50% wax coating.

²Carbopol 627, a high molecular polymer having a molecular weight of about one million supplied by B.F. Goodrich Company.

solution were withdrawn. The lead tiles were weighed to determine weight loss. The aliquots were analyzed for metals using Inductively Coupled Plasma (ICP) spectrometry. The results of each analysis are presented in Table 1 below:

5

Table 1

	pH Value	Weight loss (%)	Lead Extracted (ppm)
	7.5	0.30	170
10	8.6	0.30	155
	9.5	0.20	90
	10.5	0.07	30

Thus, as the alkalinity of the detergent compositions increased above about 10, the amount of lead extracted from the lead articles significantly decreased.

Example 2

20 It was observed that the addition of selected aluminum salts to the automatic dishwashing composition of Example 1 significantly reduced the lead extracted from the lead containing glass tiles after soaking in a detergent solution.

Detergent solutions according to Example 1 and further containing various aluminum salts to deliver 2.2 millimoles Al(III) per liter were prepared. Lead containing glass tiles were soaked in the detergent solutions under the conditions described in Example 1 except that the pH's of the detergent solutions were maintained at 8.6. After soaking, aliquots of the solutions were analyzed using ICP to determine the amount of lead extracted into the detergent solution. The results of the experiment are presented in Table 2 below:

10

Table 2

Detergent Compositions	Extracted Lead in ppm
Control (No aluminum salt)	155
Aluminum stearate	35
Aluminum acetate	35
Aluminum acetylacetonate	65
Aluminum phosphate	70

It was thus observed that the addition of aluminum salts to the low alkalinity detergent solutions significantly reduced the amount of lead extracted from the lead containing articles.

25 Example 3

To observe the effect of the presence of aluminum salts in an automatic dishwashing detergent composition, lead containing articles of having decors of various colors were washed in a dishwasher and the fading of the decor of the articles was scored.

Compositions according to Example 1 were prepared using various aluminum salts to deliver Al(III) in an amount of 2.2 millimoles Al(III) per liter in the dishwasher. A 1% solution of each of the compositions had a pH of 8.6. The following articles were washed in a Bauknecht dishwasher for 15 washes in soft water: 1 yellow plate, 1 red plate, 1 blue glass, 1 tweety glass and 1 orange glass. After the 15 washes, the articles were removed and scored for fading of decor from 0 (no fading) to 6 (substantially faded). The scored results are exhibited in Table 3 below:

Table 3

Composit ion	Yellow Plate	Red Plate	Blue Glass	Tweety Glass	Orange Glass
Control (No aluminum salt)	5	5	5	5	5
Aluminum sulfate	1	1.5	1.5	1.5	1.5
Aluminum acetate	0	0.5	1.5	0.5	2
Aluminum acetylac e-tonate	0.5	1.5	1	1.5	0.5
Aluminum ocotate	1	1.5	1.5	3	3.5
Aluminum phosphat e	4.5	3.5	4	5	5

It was observed that all the aluminum salt containing compositions exhibited less decor fading than those compositions which did not contain aluminum salts.

Example 4

It has been surprisingly found that the presence of an aluminum salt can negatively impact the removal of stains, particularly tea stain, under the conditions obtained by using these detergent compositions. This is most likely caused by a direct interaction between aluminum and the stain. It has been also surprisingly found that controlling the release of aluminum can minimize this negative impact.

10

To observe the effect of the presence of aluminum salts in an automatic dishwashing detergent composition on tea stain removal, tea stained cups and saucers were washed in the dishwasher and scored with regard to stain removal.

15

Compositions according to Example 3 were prepared using various aluminum salts to deliver Al(III) in an amount of 2.2 millimoles Al(III) per liter in the dishwasher. A 1% solution of each of the compositions had a pH of 8.6. For each experiment, eight cups and eight saucers were stained in a tea liquor and allowed to dry. Four cups and four saucers of the original eight were stained an additional three times, yielding four cups and saucers stained once, and four cups and saucers stained four times. These articles were washed one (1) time in water containing 250 ppm permanent / 320 ppm temporary hardness with the compositions described above. The scored results are exhibited in Table 4 below:

20
25

Table 4

	Composit ion	4X cup	4X saucer	1X cup	1X saucer
5	Control (No aluminum salt)	0	0	0	0
10	Aluminum sulfate	5	5	5	5
	Aluminum acetate	1	0	0	0
15	Aluminum acetylac e-tonate	3	0	1	0.75
	Aluminum octoate	0.25	0	0	0
20	Aluminum phosphat e	0.5	0	0	0

From the above, it was observed that using slow-dissolving aluminum salts (i.e. aluminum acetate, aluminum octoate and aluminum phosphate) in the wash results in the bleaching of tea stains from stained articles significantly better than using fast-dissolving aluminum salts.

Example 5

30

Another option to control the release of aluminum is by binding the aluminum to a sequestrant. Surprisingly, it has been found that this way aluminum can be prevented to interact with the stain, while still delivering its benefit of preventing lead leaching of decorated tableware.

For this option, the order of processing detergent compositions incorporating aluminum salts is critical in order to provide compositions which both effectively remove stains from articles and which inhibit extraction of minerals. To demonstrate the criticality of processing, selected cups and saucers were stained in tea, the most difficult stain to remove from tableware. Twelve cups and saucers were stained in a concentrated tea liquor, allowed to dry and then stained three additional times for a total of four tea stainings. For each of the detergent compositions described below, four cups and saucers were placed in a Bauknecht dishwasher and washed one (1) time:

Composition 1 was prepared by adding aluminum sulfate to deliver Al(III) in an amount to deliver of 0.8 millimoles Al(III) per liter in the dishwasher to the composition described in Example 1.

Composition 2 was not prepared according to the invention. Sodium citrate having pK_1 values of $pK_1=3.1$, $pK_2=4.8$ and $pK_3=6.4$ was selected as the sequestrant. Aluminum sulfate, in an amount to deliver 0.8 mM Al(III) in the wash was dosed into deionized water; during dosing, the pH of the solution was maintained at 9.5. After dosing the aluminum salt, sodium citrate to deliver 0.8 mM in the wash was added to the system. The pH of the resulting system was adjusted to 8.9 to form the premix. This premix was added to the composition described in Example 1 to generate Composition 2.

Composition 3 was prepared according to the invention. Sodium citrate in an amount to deliver 0.8 mM in the wash was completely dissolved in water; during dissolution, the pH of the solution was maintained at 9.5. Once the sequestrant completely dissolved, aluminum sulfate to deliver 0.8 mM

Al(III) in the wash was added to the solution. The pH of the resulting solution was adjusted to 8.9 to form the premix. This premix was added to the composition described in Example 1 to generate Composition 3.

5

The stained articles were evaluated for residual tea stain. A score of 0 indicated that no tea stains were observed while a score of 5 indicated that a large amount of residual tea stain on the washed articles was observed. The results are presented in Table 5 below:

Table 5

Composition	Residual Tea Stain
Composition 1-no sequestrant	5
Composition 2-incorrect premix process	4
Composition 3-correct premix process	0

20

It was thus observed that incorrect processing of the aluminum salt and sequestrant components produces an inactive premix which interferes with the removal of tea stain from washed articles.

25

Example 6

Various sequestrant materials were combined with aluminum sulfate to form a premix according to the invention and the effect of the premix on tea stain removal was observed.

30

Cups and saucers were stained as described in Example 5 above. Four samples of premix formulations were prepared to deliver 1.2 millimoles per liter of various sequestrant materials and 0.4 millimoles per liter of aluminum sulfate.

- 5 The stained articles were washed in a Bauknecht dishwasher according to Example 5 above and the washed articles were rated for residual tea stain with 0 being no stain remaining and 5 being significantly stained. The results are presented in Table 6 as follows:

10

Table 6

Composition	Cups	Saucers
15 No sequestrant/aluminum salt	5	4
Succinic acid/aluminum salt	3	0
20 Malonic acid/aluminum salt	2	0
Cyanuric acid/aluminum salt	1	0

It was thus observed that a premix of various
25 sequestrant materials and the aluminum sulfate significantly reduced tea stain on washed articles when compared to articles washed with aluminum sulfate alone.

Example 7

30

Various sequestrant materials were combined with sodium aluminate to form a premix according to the invention and the effect of the premix on tea stain removal was observed.

5 Cups and saucers were stained as described in Example 5 above. Four samples of premix formulations were prepared to deliver 1.2 millimoles per liter of various sequestrant materials and 0.4 millimoles per liter of sodium aluminate. The stained articles were washed in a Bauknecht dishwasher
10 according to Example 5 above and the

washed articles were rated for residual tea stain with 0 being no stain remaining and 5 being significantly stained. The results are presented in Table 7 as follows:

15

Table 7

Composition	Cups	Saucers
no sequestrant	5	4
20 EDTA	0	0
Sodium orthophosphate	1	0

It was thus observed that the use of a premix of
25 sequestrants with different aluminum salts according to the invention significantly reduces residual tea stain relative to the use of the aluminum salts alone.

Example 8

30

Benzoic acid was combined with aluminum sulfate at differing ratios to form a premix according to the invention. The effect of these premixes on tea stain removal was observed.

5 Cups were stained as described in Example 5. Five samples of premix formulations were prepared to deliver 0.4 millimoles per liter of aluminum sulfate at differing ratios to benzoic acid. The stained articles were washed in a Bauknecht dishwasher according to Example 5. The washed
10 articles were rated for residual tea stain with 0 being no stain remaining and 5 being significantly stained. The results are presented in Table 8 as follows:

Table 8

15

Ratio of benzoic acid to Al(III)	Cups
1 : 2	1.25
1 : 1	1.0
1.5 : 1	0
3 : 1	0

20

It was thus observed that as the ratio of benzoic acid
25 to aluminum is increased, the tea stain removal performance of the resulting premix improves.

Example 9

30 Sodium citrate was combined with aluminum sulfate to form a premix according to the invention. The percent

CLAIMS

1. An automatic dishwashing detergent composition which substantially inhibits lead corrosion of fine tableware,
5 comprising:

a) 0.01 to 25 wt. % of an aluminum salt which dissolves at a rate to deliver less than 0.56 mM aluminum(III) per minute at 42°C to a wash liquor;
10

b) 1 to 20 wt. % of a bleaching agent selected from a group of a peroxygen agent, a hypohalite agent, corresponding salts and mixtures thereof;

15 c) 1 to 75 wt. % of a builder; and

d) 0 to 40 wt. % of a surfactant,

a 1% aqueous solution of the detergent composition having a
20 pH of less than 10 and being substantially free of added silicates.

2. An automatic dishwashing detergent composition according to claim 1 wherein the aluminum salt is selected from the
25 group consisting of aluminum stearate, aluminum tartrate, aluminum acetate, aluminum acetotartrate, aluminum salicylate, aluminum bis(acetylsalicylate), aluminum formate, aluminum borate, aluminum palmitate, aluminum acetylacetonate, aluminum phosphate, aluminum octoate,
30 aluminum oleate and mixtures thereof.

3. A detergent composition according to claim 2 wherein the aluminum salts are selected from the group consisting of

aluminum acetate, aluminum acetylacetonate, aluminum octoate, aluminum phosphate and mixtures thereof.

4. A detergent composition according to claim 1 wherein the
5 aluminum salt is incorporated in the detergent composition in an amount to deliver 0.1 mM to 10 mM of aluminum(III) in the wash liquor.

5. A detergent composition according to claim 1 wherein the
10 pH of the 1% aqueous solution of the detergent composition is 7 to 9.

6. A detergent composition according to claim 1 wherein the builder is selected from inorganic or organic water soluble
15 builder salts, and mixtures thereof.

7. A detergent composition according to claim 6 wherein the organic builder is selected from a group consisting of alkali metal citrates, oxydisuccinates, polyphosphates,
20 acrylate/maleate copolymers and mixtures thereof.

8. A detergent composition according to claim 1 wherein the peroxygen agent is an organic agent or an inorganic agent.

25 9. A detergent composition according to claim 8 wherein the organic agent is selected from the group consisting of epsilon-phthalimido peroxyhexanoic acid, O-carboxybenzamidoperoxyhexanoic acid, and mixtures thereof.

30 10. A detergent composition according to claim 8 wherein the inorganic agent is selected from a group consisting of salts of monopersulfate, perborate monohydrate, perborate tetrahydrate, percarbonate and mixtures thereof.

11. A detergent composition according to claim 1 further comprising a peroxygen peracid precursor.

12. A detergent composition according to claim 11 wherein the
5 peroxygen peracid precursor is selected from a group consisting of sodium p-benzoyloxybenzene sulfonate, N,N,N',N'-tetraacetylenethylenediamine, sodium nonanoyloxybenzene sulfonate and choline sulfophenyl carbonate.

10 13. A detergent composition according to claim 1 wherein the hypohalite agent is a chloroisocyanurate.

14. A detergent composition according to claim 1 further comprising 1 to 5 wt. % enzyme selected from the group
15 consisting of a protease, an amylase, a lipase and mixtures thereof.

15. A detergent composition according to claim 1 wherein the surfactant is a nonionic surfactant.

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/EP 96/02130

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D3/39 C11D3/395 C11D3/02 C11D3/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 011 984 (S.C. JOHNSON & SON) 11 June 1980 see claims 1,2; example 3 ---	1,2,6
X	GB,A,2 172 897 (COLGATE-PALMOLIVE COMPANY) 1 October 1986 see page 9, line 45-59; claims 5,15 ---	1,2,6,8, 10-13,15
A	DATABASE WPI Week 9201 Derwent Publications Ltd., London, GB; AN 92-002750 XP002014624 & JP,A,03 255 199 (NIPPON CONTACT LENS) , 14 November 1991 see abstract --- -/--	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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- "&" document member of the same patent family

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International Application No

PCT/EP 96/02130

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 701 736 (A.E. AUSTIN ET AL.) 31 October 1972	
A	US,A,3 803 040 (F. W. GRAY) 9 April 1974	
A	US,A,3 600 317 (A.E. LINTNER) 17 August 1971	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 96/02130

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
EP-A-11984	11-06-80	US-A-	4240919	23-12-80
		AU-B-	532060	15-09-83
		AU-A-	5287679	29-05-80
		CA-A-	1123700	18-05-82

GB-A-2172897	01-10-86	US-A-	4661280	28-04-87
		AT-B-	395166	12-10-92
		AU-B-	587015	03-08-89
		AU-A-	5403186	04-09-86
		BE-A-	904315	28-08-86
		CA-A-	1291688	05-11-91
		CH-A-	668602	13-01-89
		DE-A-	3605978	04-09-86
		EG-A-	17803	30-12-91
		FR-A-	2578264	05-09-86
		HK-A-	43592	26-06-92
		JP-A-	61204300	10-09-86
		LU-A-	86334	06-10-86
		NL-A-	8600531	01-10-86
		SE-B-	466962	04-05-92
		SE-A-	8600869	02-09-86

US-A-3701736	31-10-72	BE-A-	781916	31-07-72
		CA-A-	969831	24-06-75
		CH-A-	568380	31-10-75
		DE-A-	2216657	19-10-72
		FR-A-	2132804	24-11-72
		GB-A-	1384456	19-02-75
		NL-A-	7204916	16-10-72
		SE-B-	393119	02-05-77

US-A-3803040	09-04-74	AT-A,B	312773	15-12-73
		BE-A-	767666	18-10-71
		CH-A-	561775	15-05-75
		DE-A-	2124835	09-12-71
		FR-A-	2091109	14-01-72
		GB-A-	1285845	16-08-72
		NL-A-	7107352	30-11-71
		SE-A,B,C	373874	
		CA-A-	938189	11-12-73

Information on patent family members

PCT/EP 96/02130

Form PCT/ISA/210 (patent family annex) (July 1992)